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Polyolefins Waste Materials Reconditioning Using Dissolution/Reprecipitation Method

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Abstract

Recycling of waste polymer based on low-density polyethylene (LDPE), high-density polyethylene (HDPE) or polypropylene (PP) is studied by dissolution/reprecipitation method. In this technique, Toluene and petroleum ether (PetE) as solvents with different fractions and PetE , n-hexane as non-solvents were examined at different weight percent amounts and different temperatures, using as raw material for commercial polymer products (packaging food , bags, laboratory plastic materials , detergent containers). The recovery of polymer in every case was greater than 98%. FT-IR spectra and tensile mechanical properties of the samples before and after recycling were measured. Potential recycling-based degradation of the polymer was further investigated by measuring the thermal properties (melting point, crystallinity), of the polymer before and after recycling, using DSC.

Keywords: Reconditioning, Waste, Polyolefins

1. Introduction

The produced amounts of plastic solid wastes continue to increase despite some increasing attempts to reduce, reuse, recycle and recover. This is mainly due to their wide application in the manufacture of packaging for the food industry as well as in other goods of daily life, since they do not have any side effects on the human organism. Besides that the duration of life of plastic wastes is very small (roughly 40% have

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duration of life smaller than one month). However, due to the nature of much contaminated plastic wastes they can only be partly recycled into new products. Thus, there is a vast waste stream (approximately waste generated in 2002 was 17,000 tons per day in Peninsular Malaysia) that reaches 30,000 tons per day in 2020. Therefore the plastic waste growth would be each year to the final recipients creating a serious environmental problem. Presently most used way of handling these waste streams in Malaysia is to incinerate them with energy recovery or to use them for land-filling. Economically, landfill is the best option and indeed it may be argued that landfill disposal of stable polymers can be part of responsible polymer waste management and that a certain polymer content in a landfill site contributes to its stability [1-3].

However Disposing of plastic wastes to landfill is becoming undesirable due to legislation pressures, rising costs and the poor biodegradability of commonly used polymers. In addition, incineration meets with strong societal opposition.

Therefore, re cycling either mechanical or chemical, seems to be the only route of plastic wastes management towards sustainability [1]. The dissolution of thermoplastic polymers (PE, PP, PS, PET and PVC) process plays an important role and an essential in plastics recycling which belongs to the mechanical recycling techniques [4,5]. Previous studies shows that the dissolution/precipitation the thermoplastic polymers specifically polyolefins family can be separated and reprocessed using a solvent/non-solvent system. However, differences in solubility have also been exploited for the dissolution of plastics. A suitable combination of solvents and dissolution/precipitation steps allows the main plastics to be isolated. These methods usually involve temperature variations because the solubility of a polymer in a given solvent changes drastically with this variable. This technique has been widely used by Papaspyrides et al. [6] and other researchers [5,8,9]. The main advantage of dissolution/reprecipitation over the ones applied today is that it separates mixtures of polymers without any significant decrease in the value of the polymer and it can thus be applied in treating non-homogeneous plastic waste, such as municipal waste. Pappa et al [7] were successfully applied in a pilot unit for the separation/recycling of LDPE/PP mixtures. Excellent recoveries were achieved and the quality of the recycled polymers remained practically intact. Achilias et al [5] were also investigated the dissolution/reprecipitation technique using various kind of aromatic solvents (C7-C8) with various non-solvents in recycling waste plastic packaging material. A number of polymers identified and investigated were LDPE, HDPE, PP, PS, PVC and PET.

Intend of this study is to investigate the potential of mixture of two aromatic solvents for dissolution and reconditioning polyolefin waste materials used storage containers of chemical reagent. The polymer types investigated were those typically employed in packaging applications, including LDPE, HDPE, and PP respectively and their recovery in each sample was recorded. Possible structural changes during the recycling procedure were assessed by FT-IR spectroscopy, as well as by measuring the mechanical tensile properties of the samples.

2. Experimental

2.1. Materials and Preparation of Used Polyolefin Sample

The virgin polymer as standard (LDPE, HDPE, and PP) was generously donated by Polyethylene and Polypropylene Malaysia Sdn Bhd. The chemical storage waste plastic containers used under the trade names Merck, Aldrich, and Organic, respectively for reconditioning. Solvents used toluene/petroleum ether and n-hexane), were of reagent grade purities and purchased from Merck Germany.

In this study, before small sample preparation each waste plastic container was rinse with tap water and then the waste plastic containers were cut randomly sizes into pieces between 2cm – 4cm. The sample pieces was placed in a beaker and covered with 500 ml of distilled water. Then, a beaker containing glass and

cleaning fluid was placed in a Branson ultrasonic cleaner (model 5210) water bath. Each ultrasonic-cleaning test was operated at 50 ^{o}C for 30 minutes. After ultrasonic cleaning the sample were rinse with distilled water and then placed in to vacuum oven for 6 hrs at 50 ^{o}C.

2.2. Reconditioning Technique of Polyolefin and Characterization

In order to investigate the performance of reconditioning of waste plastic, the virgin LDPE, HDPE and PP were selected as a standard. Petroleum ether/toluene blend solvent were used as solvents at ratio 1:1, and the weight ratio of blend solvent and polymer were kept at 1:15. N-hexane and petroleum were used as non-solvent for precipitation. A 1-L glass reaction vessel, fitted with high speed stirrer, reflux condenser, and thermometer, was used. The temperature was controlled by use oil bath. After assure quantitative dissolution of the polymer, the polymer solution was then filtered through filter paper of an exclusion size in the range of 20–70 mm. non-solvent was then properly added to the solution filtrate and the polymer contained was precipitated. The precipitation polymer was washed by the same non-solvent. The polymer grains were isolated by filtration under a vacuum. The reclaimed polymer was dried in a vacuum oven at 60 oC for LDPE and 80 oC For HDPE and PP for 10-15 hrs. The recycled polymer was obtained in the form of powder or grains. The chemical structure of the standard polymers and waste sample plastics before and after the restoring technique was confirmed by recording their IR spectra. The instrument used was an FT-IR spectrophotometer of Nicolt (Magna-IR560) spectrometer. The resolution of the equipment was 4 cm-1. The recorded wavenumber range was from 400 to 4000 cm-1.

3. Results and Discussion

3.1. Classification of polyolefin in waste plastic materials

In order to recognize the polymer class from which the selected used plastic material were made of, its FTIR spectra was recorded and compared to the corresponding virgin polyolefin polymer. Figures 1, 2 and 3 represents the FTIR graph of polyolefin classification. In all cases the each polymer distinct with the specific character was recognized. As it can be observed in figures in all different cases the distinguishing peaks of the waste plastic before and after recycling are almost identical to those of the parallel virgin polymer.

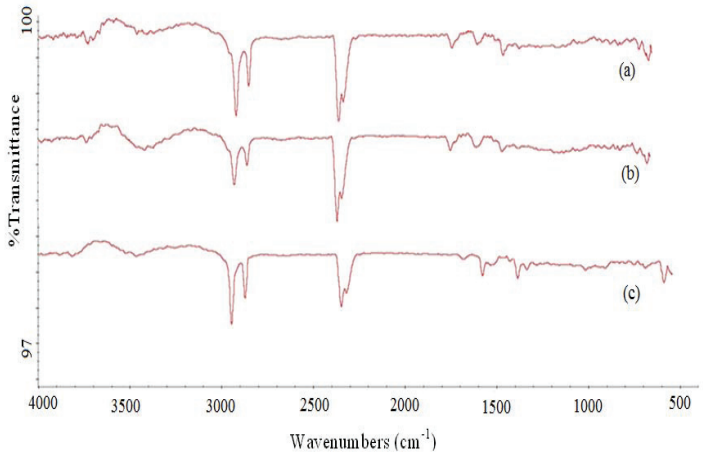

Fig. 1.Schematic diagram of FT-IR spectra of waste plastic packaging before and after recycling and virgin polymers of LDPE (a) Virgin; (b)Waste; (c) Recycled.

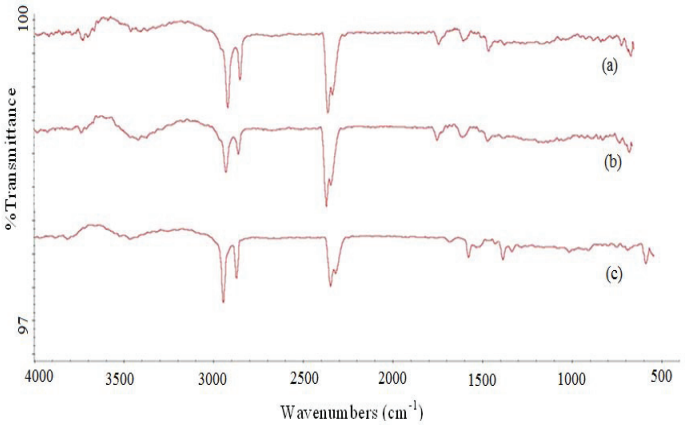

Fig. 2.Schematic diagram of FT-IR spectra of waste plastic packaging before and after recycling and virgin polymers of HDPE (a) Virgin; (b)Waste; (c) Recycled.

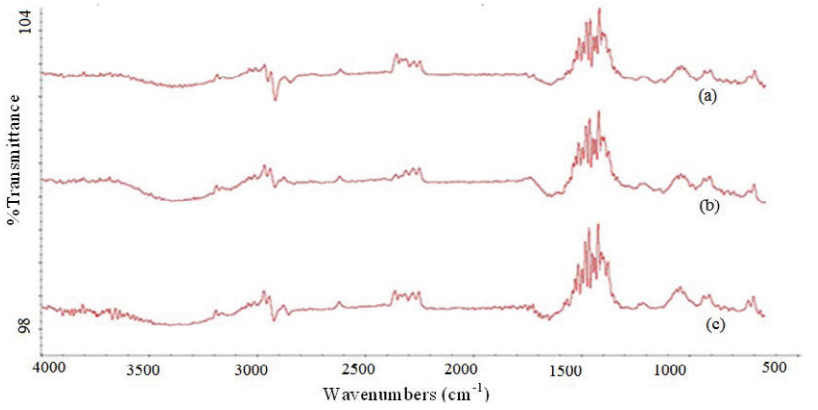

Fig. 3.Schematic diagram of FT-IR spectra of waste plastic packaging before and after recycling and virgin polymers of PP (a) Virgin; (b)Waste; (c) Recycled

3.2. Effect of Solvent system on LDPE/HDPE/PP Polymers dissolution rate

The w/v % ratio of pure and blend solvent with the polymer were kept at 1:15. Thus, taking advantage of the physical and chemical properties of LDPE, HDPE and PP, a new dissolution/precipitation processes based on various temperatures were investigated. Single solvent such as toluene, PetE(A), PetE(B), PetE(C) and blend solvent {Toluene/PetE(A), Toluene/PetE(B), Toluene/PetE(C)} system at equal amount ratio by volume, respectively were used. For precipitation process PetE and n-hexane as non-solvent were applied. Table 1 shows the polyolefin dissolution in single and blend solvent system with its fractional at various temperatures. Results revealed that by using the toluene the dissolution rate of all polymers were quite satisfactory at

various temperatures. Consequently the toluene has been proposed as sufficient solvent for the dissolution of polyolefin polymers. It was observed that the rapid dissolution rate were measured at 105°C not increasing very much with further increase in temperature (near the boiling point of the toluene). Similar performance was also observed when using the blend toluene/ PetE grade C solvent. However the dissolution rate of polymers shows insufficient when using other grade of PetE (A, & B). It is due to the low boiling (Bp.). It was concluded that the rapid dissolution of polyolefin in toluene due to the methyl group which makes it more reactive than benzene in such dissolution. However as compared to single solvent system different trend of dissolution of rate of polymers were observed when using the blend solvent system.

Table 1. Polymer (LDPE/HDPE/PP) dissolution in single and blend solvent at various temperatures

Single Solvent	Solvent Bp. °C	Dissolution Temperature (°C)			% dissolution		
		LDPE	HDPE	PP	LDPE	HDPE	PP
Toluene	110	75	100	105	100	100	100
PetE(A)	40/60	60	60	60	Zero	Zero	Zero
PetE(B)	60/80	75	75	75	Zero	Zero	Zero
PetE(C)	90/120	80	100	100	100	Zero	Zero
		Blend Solvent					
Toluene/PetE(A)	70	70	70	70	15	zero	zero
Toluene/PetE(B)	82	80	80	80	95	20	20
Toluene/PetE(C)	105	70	98	103	100	100	100

3.3. Thermal properties

Measuring for the thermal properties of the virgin polymer and waste before and after recycling was done by using (DSC Q1000 V9.6 Build 290 from TA instrument).The melting points and crystallinity it will show in Table 3. The melting point remains practically unchanged. Furthermore, crystallinity was investigated of (LDPE, HDPE and PP) for the virgin and commercials products of these polymers before and after recycling. It was observed that larger variation between the waste sample before and after recycling in all the samples based on LDPE, HDPE and PP, where it is tend to get nearer to the virgin.

Table 3. Melting temperature, Tm, and crystallinity of virgin polymers and waste polymer materials examined before and after recycling

polymer	Tm (°C)			Crystallinity %		
	virgin	Waste	Recycled	virgin	Waste	Recycled
LDPE	106	105.37	109.6	52	24.3	44.1
HDPE	134.57	129.7	130.5	77	32.08	68.2
PP	166	164.5	165.7	59	20.5	45.7

4. Conclusion

In this study an effective process were used of the recovery of waste polyolefin polymers. The reconditioning technique was investigated by using dissolution/reprecipitation process in series of single solvent and blend solvents. The polymers identified and investigated were LDPE, HDPE, and PP, respectively. The proper experimental conditions (including type of solvent/non solvent, polymer concentration, and dissolution temperature) were selected on the basis of the parallel virgin polymers. Very good polymer recoveries were obtained in almost all waste samples observed, while very low values in PetE grade A & B of all samples LDPE, HDPE and PP were attributed to the boiling limitation of host solvent and probably due to the interference of some additives present in the original waste products. From FTIR measurements it was revealed that the chemical structure was not significantly altered.

Acknowledgements

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References

[1] MPMA. “Malaysian Plastics Manufacturers Association.” www.mpma.org.my 2005.

[2] Plastics Consultancy Network–Recycling , http://www.pcn.org/

[3] C, Voûte, Why recycle. Proc. Recycling Council Annual Seminar Birmingham 1994.

[4] Hamilton, J.D. Reinert K.H. Hagan, J.V. Lord, W.V. Journal of Waste Management Association 1995;247-25.

[5] Achilias, D.S. Giannoulis, A. Papageorgiou,G. Z. Polym. Bull 2009; 63:449–465.

[6] Papaspyrides, C.D. Poulakis, J.G. Varelides, P.C. Res. Conserv. Recyc l 994; 12: 177–184.

[7] Pappa, GBoukouvalas, CGiannaris, CNtaras, N.Zografos, V.Magoulas, K.Lygeros, A.Tassios, D. The selective dissolution/precipitation technique for polymer recycling: a pilot unit application. Res. Conserv. Recyc 2001; 34: 33–44

[8] Poulakis, J.G. Papaspyrides, C.D. Res. Conserv. Recycl 1997; 20: 31–41.

[9] Poulakis, J.G. Papaspyrides, C.D. Adv. Polym. Techn 1995; 14 (3) :237–242.